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(57) Abstract

A halogenated hydantoin product, 1,3-bromochloro-5-methyl-5-propyl-hydantoin, is described which is capable of functioning as a "binder" in making pre-determined shapes, such as briquettes, tablets, flakes, granules and other compacted forms and casts of the following substrate compositions: 1,3-bromochloro-5,5-dimethylhydantoin; 1,3-dichloro-5,5-dimethylhydantoin; and 1,3-dibromo-5,5-dimethyl-hydantoin. Also described is a method whereby the briquettes, tablets, flakes, granules and other compacted forms and casts having predetermined shapes can be produced by combining the inventive composition with the substrate solid compositions, and compressing the mixture into the predetermined shape. The products are substantially dust-free solids of a desired shape having a high physical integrity and superior crush strength.

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COMPOSITIONS AND METHODS UTILIZING 1,3-BROMOCHLORO-5-METHYL-5-PROPYLHYDANTOIN

BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates to the preparation and application of 1,3-bromochloro-5-methyl-5-propylhydantoin as a "binder" in making pre-determined shapes, such as briquettes, tablets, flakes, granules, and other compacted forms and casts of 1,3-bromochloro-5,5-dimethylhydantoin ("BCDMH"), 1,3-dichloro-5,5-dimethylhydantoin ("DCDMH"), and 1,3-dibromo-5,5-dimethylhydantoin ("DBDMH"). The term "binder" is meant to refer to a compound which, when mixed with another solid compound in certain proportions, helps produce a solid which is a hard and shape-retentive structure.

Description of the Prior Art

Halogens, especially chlorine and bromine, have long been used for water treatment since they have a broad spectrum of bactericidal activity at low concentrations. Chlorine may be supplied as a pure gas from cylinders, as a liquid, or as solid hypochlorites. Dosages of these concentrated forms of chlorine are so small that sophisticated delivery devices are required for field uses. Moreover, chlorine residuals in water must be maintained within close tolerances because concentrations slightly higher than the desired range may be irritating to parts of

the human body, such as eyes, nose and skin. Further, mechanical devices which are constantly exposed to highly corrosive substances such as chlorine also may malfunction at any time, causing either a dangerously high or ineffectively low concentration of chlorine in the water.

For purposes related to the present art, chlorine is more widely used than bromine. Bromine is an excellent water disinfectant but has very limited use in the present art because pure bromine is a liquid which causes severe burns if allowed to come into contact with the skin. Moreover, its fuming vapors are highly corrosive and toxic. Further, hypobromites are not useful because, unlike hypochlorites, they are very unstable and become bromates, which are inactive as bactericides. Therefore, neither pure bromine compositions nor hypobromites are typically suitable for use.

Halogen-donating compounds are also very useful as bleaches. The oxidizing properties of compounds such as peroxygen compositions have caused such compounds to become known as good bleaching agents. However, halogen-releasing bleach compositions have greater oxidizing power than ordinary bleaches and have therefore become recognized as better bleaching agents than peroxygen compositions.

For the reasons discussed above, halogenated derivatives of 5,5-dimethylhydantoin, e.g., BCDMH, DCDMH and DBDMH, have been developed and are being used for bleaching, dishwashing, toilet bowl disinfection and water treatment application such as cooling water treatment and spa and swimming pool disinfection. These halogen donors are manufactured in fine powder or in "dust" forms. However, the physical nature of a halogen donor often plays a significant role in its use. Therefore, there is an urgent need for halogen donors available in the form of dust-free briquettes, tablets, flakes and granules.

Halogen donor compounds such as BCDMH, DCDMH and DBDMH

are irritating in nature. Since these products exhibit a large amount of dusting, they are undesirable for use in and around the home, as well as in industrial environments for bleaching, dishwashing or other purposes. Additionally, a high dusting product tends to intensify the halogen odor normally associated with halogen donor compounds. Such a halogen odor can, in and of itself, be most irritating, and should be avoided.

Research in the field of halohydantoin production has focused in a large degree upon developing ways to eliminate the dusting problem and other problems associated with halogenated 5,5-dimethylhydantoins and 5-ethyl-5-methyl-hydantoins in their pure dust forms. For instance, in U.S. Patent No. 4,242,216, Dougherty et al. disclosed that DCDMH is not capable of being stored substantially stably in contact with alkaline powdered formulations until after it has been compacted and broken up into fragments of "specific screen sizes". However, this is problematic because, as fine, dusty powders, halogenated derivatives of dimethylhydantoin are difficult to compact into solid forms of high integrity or to granulate. The process disclosed in the Dougherty et al. patent to compact dimethylhydantoins requires a preferred pressure of between 30,000 and 40,000 psi.

Other research has been performed in this field to provide better and more efficient ways to transform halohydantoins from powder to more shape-retentive forms. Patterson illustrated in U.S. Patent No. 3,412,021 that polyvalent metallic cations such as aluminum, zinc, tin, iron, chromium, magnesium, and silicon can be used as binders for BCDMH, DCDMH or DBDMH. However use of these cations is rather expensive and, therefore, the cost of the final product is unduly high. Moreover, these binders do not prevent dusting problems.

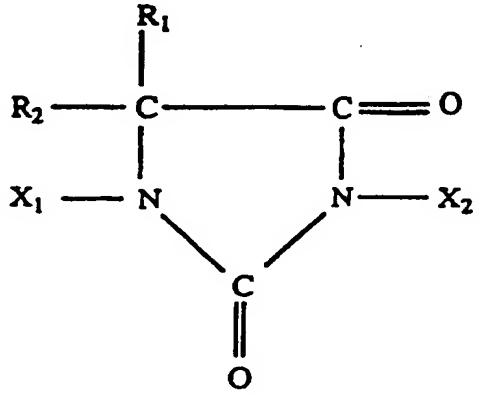
Girard et al. attempted to solve some of these problems

by disclosing methods in U.S. Patent No. 4,560,766 whereby dihalogenated-5,5-diethylhydantoins and dihalogenated-5,5-ethylmethylhydantoins were formed into a definite shape either as "the sole constituent or in admixture with halogenated dimethylhydantoins." Said patent discloses formation of the shapes either by compacting or by melting the object substance and pouring it into forms. The invention of Girard et al. relied upon the fact that diethyl- and ethylmethylhydantoins have a greater disparity between their respective melting points and decomposition points than do dimethylhydantoins. Therefore, the former were more easily melted and formed than the latter. However, Girard et al. did not disclose any other halogenated-5,5-dialkylhydantoins, nor did they claim the use of diethyl- or ethylmethylhydantoin as a "binder" in BCDMH, DCDMH or DBDMH.

SUMMARY OF INVENTION

Although halohydantoin chemistry is well known and understood in the prior art, heretofore no one has discussed 1,3-bromochloro-5-methyl-5-propylhydantoin ("BCMPH") and its unique characteristics. Specifically, when this compound is mixed with other dust-forming halohydantoins and the mixture composition is compressed into a desired shape, the BCMPH acts as a binder to hold the solid products into the desired shape.

Briefly describing one aspect of the present invention, there is provided a hard and shape-retentive composition, useful in providing desired dosages of halogens in water for long periods of time without substantial loss of potency. The composition is a mixture of a well-known halogenated hydantoin represented by the following formula:



in which each of X_1 and X_2 is selected from the group consisting of chlorine and bromine, and each of R_1 and R_2 is an alkyl group having one or two carbon atoms; combined with 1,3-bromochloro-5-methyl-5-propylhydantoin.

Another aspect of the present invention is a method for making a hard and shape-retentive composition by (1) forming

a mixture of the two compounds described above, and (2) processing the mixture into the desired shape.

It is an object of the present invention to provide a way in which briquettes, tablets, flakes, granules, and other compacted forms and casts of halogenated hydantoins can be more economically generated. Such compacted products are useful for the purpose of immersing them in water for long periods of time without substantial loss of potency of their active product.

Another object of the invention is to provide a composition and a method by which briquettes, tablets, flakes, granules and other compacted forms and casts of halogenated hydantoins can be generated which have a substantially greater "crush strength."

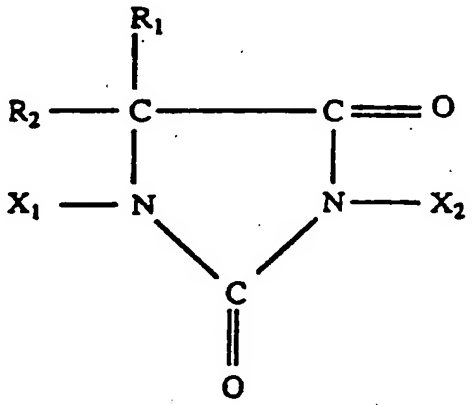
A further object of the invention is to utilize a novel halogenated hydantoin, 1,3-bromochloro-5-methyl-5-propyl-hydantoin, as a "binder" due to its unique chemical and physical properties.

Further objects and advantages of the present invention will be apparent from the following description.

DESCRIPTION OF THE PREFERRED EMBODIMENT

For the purposes of promoting an understanding of the principles of the invention, reference will now be made to the preferred embodiment of the invention and specific language will be used to describe the same. It will nevertheless be understood that no limitation of the scope of the invention is thereby intended, such alterations, modifications and further applications of the principles of the invention being contemplated as would normally occur to one skilled in the art to which the invention relates.

The hard and shape-retentive compositions of this invention are mixtures of two halogenated hydantoins. The mixtures comprise (1) a halogenated hydantoin represented by the following formula:



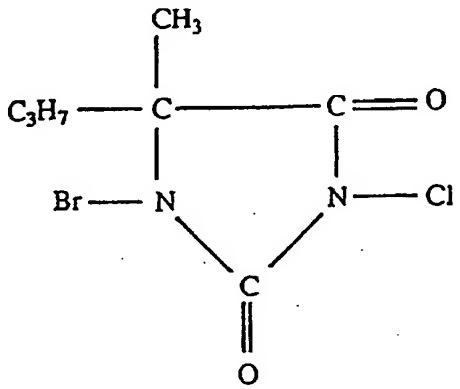
in which each of X_1 and X_2 is selected from the group consisting of chlorine and bromine, and each of R_1 and R_2 is an alkyl group having one or two carbon atoms; and (2) 1,3-bromochloro-5-methyl-5-propylhydantoin ("BCMPH").

Halogenated hydantoins are well known in the prior art as having good halogen donating ability and, therefore,

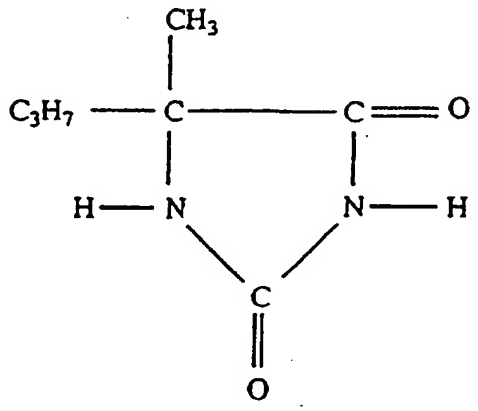
being useful for water treatment applications. All of these halogen donors are manufactured as a fine powder, or in "dust" forms. Since the physical nature of a halogen-donating substance often plays a significant role in its use, there has been an urgent need for such halogen donors to be available in the form of briquettes, tablets, flakes, granules and other compacted forms particularly with reduced dusting.

The present invention utilizes BCMPH as a binder for other halogenated hydantoins and enables the formation of superior compacted forms having reduced dusting. Although, several unknown N-monohalogenated- or N,N-dihalogenated-5,5-dialkylhydantoins were prepared and screened, only the composition of BCMPH was found to have the proper chemical and physical properties. In particular, BCMPH has been found to be compatible with certain other halogenated hydantoins, and has a melting point of 56-65°C, which makes the BCMPH effective as a "binder" in the briquetting of the other, halogen-donating dimethyl-hydantoins. In addition the BCMPH will also serve as a halogen donor, further enhancing the utility of the product.

1-Bromo-3-chloro-5-methyl-5-propylhydantoin is represented by the following formula:



Regarding the preparation of BCMPH, the starting hydantoin represented by the following formula:



is prepared, for example, by the well-known Bucherer-Bergs synthesis using potassium cyanide, ammonium carbonate (or ammonium bicarbonate) and methyl propyl ketone, in ethanol-water (50:50 v/v), either at atmospheric pressure or under greater than atmospheric pressure.

Further, preparations of bromochlorohydantoins are also well known. The standard method of making mixed halogenated organic products is to halogenate stepwise: isolating the product and subjecting the obtained product to the next halogenation step, and so on. By modification of the method applicable to preparing N-halo organic heterocyclic compounds, it is possible to prepare the mixed 1,3-dihalo-5,5-dialkyl-hydantoins. The method can be carried out by treating one mole of the 5-methyl-5-propylhydantoin in water in the presence of NaOH with one-half of a mole of bromine, and then chlorinating the resulting mixture to produce the desired 1,3-bromochloro-5-methyl-5-propylhydantoin.

Under these conditions, the initial one-half mole of bromine will introduce one bromine in one-half mole of the 5,5-dialkylhydantoin and will also form one-half of a mole of NaBr. When chlorine is passed, it will liberate bromine from NaBr which will then brominate the other (non-brominated) half mole of the hydantoin. One mole of chlorine will then be required to chlorinate the remaining N-H group of the hydantoin. The final product, thus obtained, is 1,3-bromochloro-5,5-dialkylhydantoin.

The other starting materials, 1,3-bromochloro-5,5-dimethyl-hydantoin ("BCDMH"), 1,3-dichloro-5,5-dimethylhydantoin ("DCDMH"), and 1,3-dibromo-5,5-dimethylhydantoin ("DBDMH"), are available commercially. These compounds can be prepared by the same method, wherein the methyl propyl ketone in the initial step is substituted with dimethyl ketone and the halogenation step is accomplished either by the method above or by other halogenation methodology that is well known in the prior art.

"Briquetting" is the process by which the starting materials, BCDMH, DCDMH, DBDMH and BCMPH, are compacted into various shapes and sizes such that their physical state changes from a powder to a hard and shape-retentive form. Compactability of a material is a function of "crush strength." The halogen donor compositions BCDMH, DCDMH and DBDMH are all manufactured and available in fine powder, or "dust" forms. The addition of non-halogen-donating substances to these halogenated hydantoins has been used in the prior art to accomplish briquetting by reasonable compacting procedures. However, the present invention provides for a mixture of two halogenated hydantoins, and allows for the production of briquettes or other forms without the addition of non-halogen-donating substances. The present invention also provides a composition and method

whereby the crush strength of the resulting product is substantially greater than that of the pure halogenated hydantoins of the prior art. Further, the present invention provides a composition and method whereby the product does not have the "dusting" problem of the halogen donating compositions of the prior art.

The use of BCMPH as a binder is effectively accomplished at mixture compositions of from 0.1 to 10.0 weight% of BCMPH in DCDMH, DBDMH, and BCDMH; more preferably from 1.0 to 5.0 weight%; and most preferably about 2.5 weight%. During the briquetting process, there will be a significant rise of temperature, but this rise in temperature is not so severe that it causes decomposition of the hydantoin materials being compressed. In view of the fact that other halohydantoins do not have similar binding utility, it is apparant that BCMPH has unique chemical and/or physical properties which make it effective as a binder for the other halogen-donor hydantoins. One property may be the similar physical structure, and therefore compatibility. It also appears that the BCMPH melts during the briquetting process, and then resolidifies, thus perhaps providing binding strength and anti-dusting qualities to the briquettes as a result. Other physical or chemical activity or characteristics may also be involved.

The invention will be further described with reference to the following specific Examples. However, it will be understood that the Examples are offered to further illustrate the present invention, but are not to be construed as limiting the scope thereof.

EXAMPLES 1-6

Preparation of 5-Methyl-5-alkylhydantoin

A mixture of methyl alkyl ketone (1.0 M), ammonium

carbonate (2.37 M), and potassium cyanide (1.08 M) in water or ethanol-water (50:50 v/v) (15:1 v/w on ketone) was heated under stirring at 100°C/35 psi for 5-6 hours. The cooled reaction mixture was acidified to pH 4.5 with HCl at ambient temperature. The precipitated solid was filtered and the cake was washed repeatedly with water until the washing was halogen free. The yields and properties of the 5,5-dialkylhydantoins prepared according to this method are given below in Table I.

TABLE I

(Yields and properties of 5, 5-Dialkylhydantoins)

Compound	Yield,%	M.P. °C		GC Assay,
		Found	Literature	Area%
Methyl propylhydantoin	98.9	124-25	124-25	99.6
Methyl isobutylhydantoin	71.2	144-46	144-46	100.0
Methyl pentylhydantoin	69.6	101-03	101-03	99.3
Methyl heptylhydantoin	93.8	102-04		93.8
Methyl hexylhydantoin	89.7	107-08	107-08	99.7
Methyl octylhydantoin	96.2	106-08		100.0

EXAMPLE 7

Preparation of 1,3-Bromochloro-5-methyl-5-propylhydantoin (BCMPH)

To a 1000 ml, 6-neck flask equipped with an agitator, a thermometer, dropping funnel (subsurface), chlorine inlet-tube (subsurface), pH electrode, dropping funnel for aqueous NaOH solution and condenser were charged 62.4 g (0.4 mole) of 5-methyl-5-propylhydantoin (MPH), and 260 ml of water. To the suspension were added 28.8 g (0.18 mole) of bromine and the required quantity of aqueous NaOH solution (25 wt%) simultaneously at a pH of about 7 at about 25°C during five minutes. After complete addition, the suspension was stirred for 10 minutes more. Chlorine (50.6 g) and the required quantity of aqueous NaOH solution (25 wt%) were then introduced into the suspension simultaneously at a pH of about 7 and at a temperature of about 25°C. The resulting suspension was stirred for another 30 minutes. The product was then filtered, washed with water until it was free of halogen and dried <u>in vacuo</u> over anhydrous $CaCl_2$. The BCMPH was obtained as a white solid melting at 56-65°C. The yield of BCMPH was 90.7% (on MPH). Anal. Calcd. For $C_7H_{10}BrClN_2O_2$:Br, 29.7%; Cl, 13.2%. Found: Br, 27.6%; Cl, 13.6%. TOP (total oxidizing power),

97.2%, NMR Analysis: DCMPH (dichloro-MPH), 24.5%; BCMPH, 54.0%; DBMPH (dibromo-MPH), 21.5%.

EXAMPLE 8

Preparation of Briquettes from Halohydantoin Mixtures

The BCMPH prepared in Example 7 is mixed with BCDMH to prepare a loading composition of 2.5% BCMPH and 97.5% BCDMH by weight. This composition is mixed thoroughly and loaded into a briquetting machine. In the briquetting machine, the solid mixture is compacted into briquettes of predetermined size and shape.

EXAMPLE 9

Chemical Mixture of BCDMH (90%) & BCMPH (10%) *In Situ*

In an apparatus similar to that used in Example 7 were charged 77.9 g (0.6 mole) of 5,5-dimethylhydantoin (DMH) and 10.6 g (0.07 mole) of 5-methyl-5-propylhydantoin (MPH) and 453 ml water. To the suspension was added 44.8 g (0.28 mole) of bromine at a pH of about 7 at 25°C, followed by 81.1 g (1.14 moles) of chlorine under identical conditions. The BCDMH and BCMPH product, thus obtained, was an off-white solid in 77.1% yield with a melting point of 144-147°C. Anal. Calcd.: Br, 32.7%; Cl, 14.5%. Found: Br, 32.3%; Cl, 14.6%. TGA Loss: 5% at 121.7°C; 25% at 150.0°C and 50%, at 166.9°C.

EXAMPLE 10

Preparation of Briquettes from Mixture Prepared *In Situ*

The chemical mixture of BCDMH and BCMPH prepared *in situ* in Example 9 is loaded into a briquetting machine as in Example 8. In the briquetting machine, the mixture is compacted into briquettes of predetermined size and shape.

EXAMPLE 11

Products are prepared by mixing various halogenated dimethylhydantoins, including DCDMH and DBDMH, with BCMPH as in Example 8. Further, products are prepared utilizing various percentages of BCMPH in the mixtures prepared for briquetting. Preferred mixtures contain from 0.1 to 10.0 weight percent of BCMPH.

EXAMPLE 12

Products are formed into various solid shapes such as tablets, flakes and granules using the procedures described in Example 8 and Example 10, and in accordance with well known processes in the art, suitable products are obtained.

EXAMPLE 13

To determine the optimal ratio of BCMPH in mixtures containing BCMPH and BCDMH, the general method of Example 8 was used, varying only the loading compositions, to compact mixtures containing 0 wt %, 1.0 wt %, 2.5 wt % and 5.0 wt % of BCMPH. As is shown by the results in Table II, the optimal composition contains 2.5 wt % BCMPH, and this

composition exhibits nearly double the crush strength of pure BCDMH without the inventive binder composition.

TABLE II

BCMPH Loading	Crush Strength	Product Rate	Productio Rate
% w/w	psi	%	lbs/hr
0.0	13.6	75.5	58.5
1.0	20.0	73.6	61.0
2.5	26.7	82.7	74.1
5.0	26.8	80.4	36.3

While the invention has been illustrated and described in detail in the foregoing description, the same is to be considered as illustrative and not restrictive in character, it being understood that only the preferred embodiment has been shown and described and that all changes and modifications that come within the spirit of the invention are desired to be protected.

What is claimed is:

1. The composition of claim 26 in which each of X_1 and X_2 is bromine and each of R_1 and R_2 is a methyl group.

2. The composition of claim 1 in which the 1,3-bromochloro-5-methyl-5-propylhydantoin is from 0.1 wt% to 10.0 wt% of the mixture.

3. The composition of claim 2 in which the 1,3-bromochloro-5-methyl-5-propylhydantoin is from 1 wt% to 5 wt% of the mixture.

4. The composition of claim 3 in which the 1,3-bromochloro-5-methyl-5-propylhydantoin is about 2.5 wt% of the mixture.

5. The composition of claim 26 in which each of X_1 and X_2 is chlorine and each of R_1 and R_2 is a methyl group.

6. The composition of claim 5 in which the 1,3-bromochloro-5-methyl-5-propylhydantoin is from 0.1 wt% to 10.0 wt% of the mixture.

7. The composition of claim 6 in which the 1,3-bromochloro-5-methyl-5-propylhydantoin is from 1 wt% to 5 wt% of the mixture.

8. The composition of claim 7 in which the 1,3-bromochloro-5-methyl-5-propylhydantoin is about 2.5 wt% of the mixture.

9. The composition of claim 26 in which one of X_1 and X_2 is bromine and the other of X_1 and X_2 is chlorine, and in which each of R_1 and R_2 is a methyl group.

10. The composition of claim 9 in which the 1,3-bromochloro-5-methyl-5-propylhydantoin is from 0.1 wt% to 10.0 wt% of the mixture.

11. The composition of claim 10 in which the 1,3-bromochloro-5-methyl-5-propylhydantoin is from 1 wt% to 5 wt% of the mixture.

12. The composition of claim 11 in which the 1,3-bromochloro-5-methyl-5-propylhydantoin is about 2.5 wt% of the mixture.

13. The method of claim 28 in which each of X_1 and X_2 is bromine and each of R_1 and R_2 is a methyl group.

14. The method of claim 13 in which the 1,3-bromochloro-5-methyl-5-propylhydantoin is from 0.1 wt% to 10.0 wt% of the mixture.

15. The method of claim 14 in which the 1,3-bromochloro-5-methyl-5-propylhydantoin is from 1.0 wt% to 5.0 wt% of the mixture.

16. The method of claim 15 in which the 1,3-bromochloro-5-methyl-5-propylhydantoin is about 2.5 wt% of the mixture.

17. The method of claim 28 in which each of X_1 and X_2 is chlorine and each of R_1 and R_2 is a methyl group.

18. The method of claim 17 in which the 1,3-bromochloro-5-methyl-5-propylhydantoin is from 0.1 wt% to 10.0 wt% of the mixture.

19. The method of claim 18 in which the 1,3-bromochloro-5-methyl-5-propylhydantoin is from 1.0 wt% to 5.0 wt% of the mixture.

20. The method of claim 19 in which the 1,3-bromochloro-5-methyl-5-propylhydantoin is about 2.5 wt% of the mixture.

21. The method of claim 28 in which one of X_1 and X_2 is bromine and the other of X_1 and X_2 is chlorine, and in which each of R_1 and R_2 is a methyl group.

22. The method of claim 21 in which the 1,3-bromochloro-5-methyl-5-propylhydantoin is from 0.1 wt% to 10.0 wt% of the mixture.

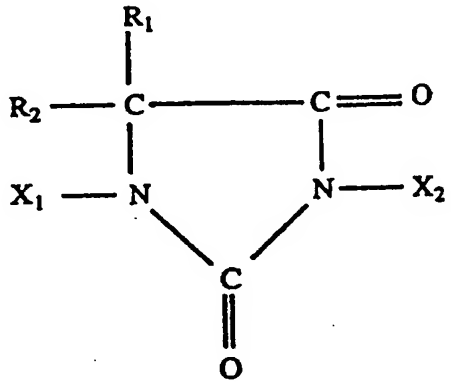
23. The method of claim 22 in which the 1,3-bromochloro-5-methyl-5-propylhydantoin is from 1.0 wt% to 5.0 wt% of the mixture.

24. The method of claim 23 in which the 1,3-bromochloro-5-methyl-5-propylhydantoin is about 2.5 wt% of the mixture.

25. The method of claim 28 wherein said providing step comprises preparing said 1,3-bromochloro-5-methyl-5-propyl-hydantoin and said halogenated hydantoin together as a chemical mixture made *in situ*.

26. A hard and shape-retentive composition, useful in providing desired dosages of halogens in water for long periods of time without substantial loss of potency, comprising a mixture of:

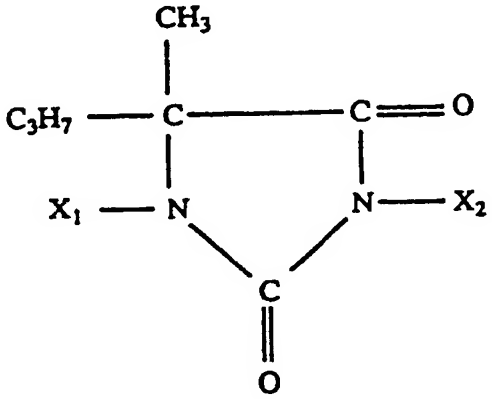
a. one or more halogenated hydantoins represented by the following formula:



in which each of X_1 and X_2 is selected from the group consisting of chlorine and bromine, and each of R_1 and R_2 is an alkyl group having one or two carbon atoms; and

b. 1,3-bromochloro-5-methyl-5-propylhydantoin.

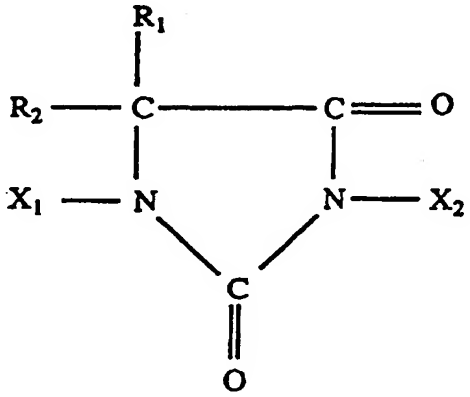
27. The composition 1,3-bromochloro-5-methyl-5-propyl-hydantoin represented by the following formula:



wherein one of X_1 and X_2 is bromine and the other of X_1 and X_2 is chlorine.

28. A method for generating a hard and shape-retentive composition, useful in providing desired dosages of halogens in water, comprising:

a. providing a mixture of (i) a halogenated hydantoin represented by the following formula:



in which each of X_1 and X_2 is selected from the group consisting of chlorine and bromine, and each of R_1 and R_2 is an alkyl group having one or two carbon atoms, and (ii) 1,3-bromochloro-5-methyl-5-propylhydantoin, and;

b. compressing the mixture into the desired shape at a temperature at or above the melting temperature of 1,3-bromochloro-5-methyl-5-propylhydantoin but below its decomposition temperature.

29. The product obtained by the method of claim 32.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US97/08162

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :C07D 233/40, 233/78, 233/84, 233/86
US CL :548/320.5
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 548/320.5

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Please See Extra Sheet.

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

NONE

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 3,147,252 X (PATERSON) 01 September 1964, see entire document.	27
Y	US 5,560,766 X (GIRARD ET AL) 24 December 1985, see entire document.	1-32

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

*	Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	document defining the general state of the art which is not considered to be of particular relevance	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E"	earlier document published on or after the international filing date	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&"	document member of the same patent family
"O"	document referring to an oral disclosure, use, exhibition or other means		
"P"	document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search 14 AUGUST 1997	Date of mailing of the international search report 11 SEP 1997
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3230	Authorized officer FLOYD D. HIGEL Telephone No. (703) 308-1235

Form PCT/ISA/210 (second sheet)(July 1992)*

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US97/08162

B. FIELDS SEARCHED
Documentation other than minimum documentation that are included in the fields searched:

Chemical Abstract Beilstein, Vols 17 to 27
Current Abstracts of chemistry
Index Chemicus